

## Controlled radical polymerization of styrene utilizing excellent radical capturing ability of diphenyl ditelluride

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### Summary

The radical polymerization of styrene was investigated in the presence of diphenyl ditelluride (**DPDTe**) under varied conditions. In the polymerization without any radical initiator at higher temperature (125°C), the addition of **DPDTe** surely decreased the polymer molecular weight ( $M_n$ ) while the polydispersity ( $M_w/M_n$ ) was rather broad. The polymerization with benzoyl peroxide (BPO) as the initiator was also uncontrollable to afford polymers with broad  $M_w/M_n$  probably due to the redox side reaction of BPO with **DPDTe**. On the contrary, the precision control of  $M_n$  and the initiating end structure could be achieved by the polymerization with 2,2'-azobisisobutyronitrile (AIBN), that is,  $M_n$  increased in proportion to the molar ratio of monomer to initiator suggesting the suppression of bimolecular chain termination reactions by the excellent radical capturing ability of **DPDTe**.

### Introduction

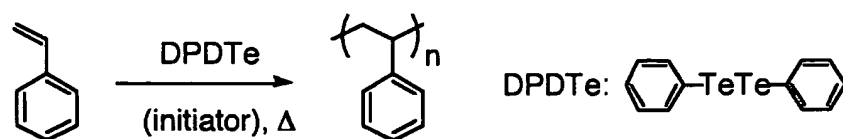
The control of macromolecular structure such as molecular weight, polydispersity, end group functionality, component, and their architecture is of great important subject not only in the synthetic polymer chemistry but also in their commercial utilization. Living polymerization technique might be one of the most reliable methodologies to attain this purpose and numerous living systems based on ionic [1], ring opening metathesis [2], and group transfer polymerizations [3] were developed giving rise to well-defined polymers from specified monomers. In contrast to aforementioned techniques, radical polymerizations are rather tolerant to moisture and polar substituents in monomer to enable to afford wide variety of polymeric materials, however, traditional radical polymerizations frequently suffer from bimolecular chain terminations to give unpredictable structure. Iniferter mechanism proposed by Otsu et al. [4] was followed by the subsequent controlled radical polymerizations, such as the permanent nitroxyl radical (namely, TEMPO) mediated stable free-radical polymerization (SFRP) introduced by Rizzardo et al. [5]. Another strategy by virtue of transition metal catalyzed redox reactions, termed as atom transfer radical polymerization (ATRP), were developed by Sawamoto et al. (Ru system) [6] and Matyjaszewski et al. (Cu system) [7], which have their roots in organic chemistry's

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atom transfer radical addition (ATRA) [8]. In those cases, the concentration of the propagating radical must be suppressed to the utmost by the dynamic equilibrium between dormant and active species promoted by the thermally or photolytically labile C-S and C-O bond and the redox active C-halogen bond scission.

Organic chalcogenides have recently drawn much attention in their contribution to the radical chemistry, especially in the homolytic substitution at chalcogen atoms [9], where the excellent radical affinity of chalcogenides enables the intra or intermolecular carbon-hetero atom bond construction [10]. Sulfur compounds have been often played an important role in radical polymerization chemistry, whereas selenium and tellurium compounds related polymerizations are less explored. From these viewpoints, we have recently reported the radical photopolymerization of styrene with some selenium compounds [11]. Herein, the controlled radical polymerization of styrene was demonstrated by utilizing **DPDTe** taking advantage of the more excellent radical capturing ability of tellurium than that of selenium compounds [12] (Scheme 1).

**Scheme 1.**



### Experimental section

**Materials and instruments** Diphenyl ditelluride (**DPDTe**) was synthesized and purified according to the previously reported procedure [13]. Styrene was washed with aq. NaOH to remove inhibitors, then with water, dried over  $\text{CaH}_2$ , and distilled before use. Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) were recrystallized from EtOH.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a JEOL JNM-GX400 instrument (tetramethylsilane as an internal standard). IR spectra were obtained on a NICOLET Impact 400D spectrometer. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh DP-8020 (TSK gel MultiporeH<sub>XL</sub>-M, THF as an eluent) on the basis of standard polystyrene samples. MALDI-TOF-Mass experiments were carried out on a PerSeptive Biosystems Inc., Voyager-DE mass spectrometer. A nitrogen laser (337nm, 3kW peak laser power) was used to desorb the sample ions. The instrument was operated in linear delayed-extraction mode with an accelerating potential of 20kV. Raw data was analyzed with Grams386 software. Samples for MALDI-TOF mass spectroscopic analyses were prepared by mixing 10 $\mu\text{L}$  of the matrix solution ( $\alpha$ -cyano-4-hydroxy-cinnamin acid ( $\alpha\text{CHCA}$ ) (9.7mg in 0.5mL of THF)) containing silver trifluoroacetate as a cationization reagent and 10 $\mu\text{L}$  of the polymer solution (2.3mg in 0.5mL of THF) on the surface of a stainless steel, which was introduced into the laser desorption chamber.

**Reaction of BPO with DPDTe** A mixture of BPO 0.017g (0.07mmol), **DPDTe** 0.057g (0.14mmol), and benzene (3mL) was stirred under nitrogen at room temperature for 24h in a test tube covered with aluminum foil. The solution gradually turned into deep-green color accompanied by the precipitation of tellurium metal. After the reaction mixture was in vacuo, IR spectrum was directly corrected. IR (KBr disk,  $\text{cm}^{-1}$ ): 1645 and 1637 ( $\nu_{\text{C=O}}$ ), 1315 and 1295 ( $\nu_{\text{C-O}}$ ), 680 and 559 ( $\nu_{\text{Te-O}}$ ).

**Typical polymerization procedure (in sealed tube)** To a grass tube containing a magnetic stirrer bar, AIBN 0.07g (0.44mmol), and **DPDTe** 0.36g (0.87mmol), was added styrene 0.90g (8.7mmol) and the mixture was degassed several

times by freeze-pump-thaw cycles. The tube was then sealed under vacuum and the polymerization was conducted in an oil bath at 90°C with the tube covered by aluminum foil. After the content turned into solid (ca. for 36h), the polymerization mixture was dissolved in THF (5mL) and precipitated into MeOH (200mL) several times to obtain a polymer (0.80g) in 89% yield. <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ (ppm) 0.90-1.20 (-CH<sub>3</sub>), 1.30-1.70 (-CH<sub>2</sub>-), 1.70-2.50 (-CHPh-), 6.30-7.80 (aromatic)

**Typical polymerization procedure (under nitrogen atmosphere)** A test tube containing a magnetic stirrer bar, AIBN 0.07g (0.44mmol), and DPDTe 0.36g (0.87mmol) was closed by a three-way stopcock and placed under nitrogen by repeating several times a vacuum-nitrogen cycle. Styrene 0.90g (8.7mmol) was then added under nitrogen with syringe. The polymerization was conducted in a similar way to that in sealed tube to obtain a polymer (0.71g) in 79% yield.

## Results and discussion

**Polymerization without radical initiator** The polymerization of styrene was performed for 36h in the presence of DPDTe without radical initiator. As can be seen in Table 1, the polymerization did not proceed at 90°C (run 1) suggesting that the DPDTe does not initiate the radical polymerization of styrene under these conditions [14]. Another possibility that the conjectural carbon-tellurium bond at the propagating end never cleave to result in chain termination can be excluded because a polymer could be obtained in AIBN/DPDTe binary system at 90°C (*vide infra*). The polymerization at higher temperature (125°C) proceeded to give polymers in high yields (runs 2-5) and both the polymer molecular weight ( $M_n$ ) and the polydispersities ( $M_w/M_n$ ) were effected by the concentration of DPDTe, which means that the addition of DPDTe altered the radical concentration and/or the radical activity generated by the spontaneous initiation mechanism proposed by Mayo [15].

**Table 1.** Polymerization of styrene in the presence of DPDTe without radical initiator

run	DPDTe (mol%)	temp. (°C)	yield (%) <sup>a</sup>	$M_n$ <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
1	10	90 <sup>c</sup>	trace	—	—
2	10	125	87	22 100	1.55
3	5	125	86	30 700	1.71
4	2.5	125	86	39 700	1.66
5	1	125	87	46 700	1.96

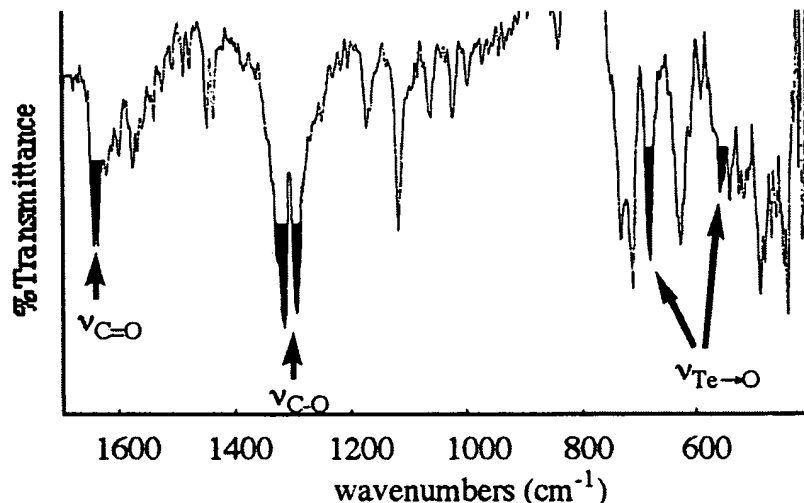
<sup>a</sup> Isolated yield after reprecipitation into MeOH. <sup>b</sup> Estimated by GPC (THF, PSt standard).

<sup>c</sup> Polymerization was carried out for 36h.

**Polymerization with radical initiator** As the molecular weight and the end structure of the polystyrene obtained without radical initiator were uncontrollable, DPDTe was then used in combination with common radical initiators. At the beginning, BPO/DPDTe system was investigated for the polymerization of styrene at 95°C, however, no polymer was obtained after 20h and the precipitation of tellurium metal was observed at the early stage of the polymerization.

To elucidate this phenomenon in detail, a benzene solution of BPO and DPDTe was stirred under nitrogen for 24h in darkness to find out that DPDTe might be

oxidized by BPO to give rise to various tellurium compounds such as  $\text{PhTe}(\text{OCOPh})_3$ ,  $\text{Ph}_2\text{Te}(\text{OCOPh})_2$ ,  $\text{PhTe}(\text{O})\text{OCOPh}$ ,  $\text{PhTe}(\text{O})\text{OTe}(\text{O})\text{Ph}$ , etc. judging from the peaks in IR spectrum of the reaction mixture (Figure 1) [16]. Accordingly, the radical initiation by BPO was supposed to be inhibited by the redox side reaction.



**Figure 1.** IR spectrum of reaction mixture of BPO with DPDTe (KBr Disk)

Similar polymerization by BPO/DPDTe was again carried out at higher temperature (125°C) to obtain a polymer, but thus obtained polymer had broad polydispersities and no aromatic peak assignable to the BPO fragment at the initiating end was detected in  $^1\text{H-NMR}$  spectrum, which means the polymerization was initiated not by BPO but spontaneously.

Hence, the polymerization with AIBN/DPDTe binary system was then conducted because AIBN are considered not to occur any redox reaction. First of all, the polymerization condition was optimized by changing the  $[\text{DPDTe}]/[\text{AIBN}]$  ratio. As a result, smaller  $M_n$  as well as narrower  $M_w/M_n$  could be attained and the polymerization rate significantly decreased in the presence of excess amount of DPDTe (Table 2).

**Table 2.** Radical polymerization of styrene under various  $[\text{DPDTe}]/[\text{AIBN}]$  ratio <sup>a</sup>

run	$[\text{DPDTe}]/[\text{AIBN}]$	yield (%) <sup>b</sup>	$M_n$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
1	0	90	16 000	2.46
2	0.5	95	9 500	1.26
3	1.0	93	8 200	1.22
4	2.0	86	6 200	1.18
5 <sup>d</sup>	—	trace	—	—

<sup>a</sup> Conditions;  $[\text{St}]=8.7\text{mmol}$ ,  $[\text{AIBN}]=0.15\text{mmol}$ , at 90°C for 36h.

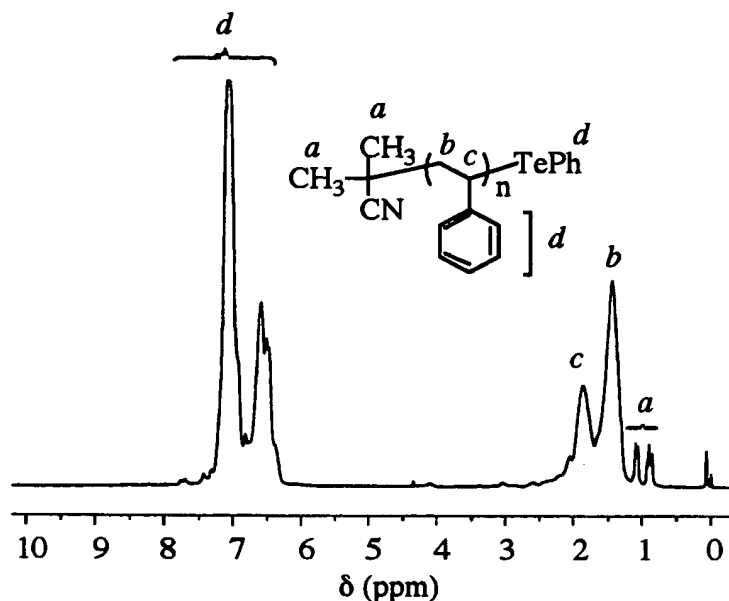
<sup>b</sup> Isolated yield after reprecipitation into MeOH. <sup>c</sup> Estimated by GPC (THF, PSt standard).

<sup>d</sup> Polymerization was carried out without AIBN.  $[\text{St}]/[\text{DPDTe}]=100$ .

It should be noted that  $M_n$  (6 200) in run 4 indicated higher initiation efficiency (ca. 84%) of AIBN compared to conventional value (60-70%) without DPDTe [17]. The

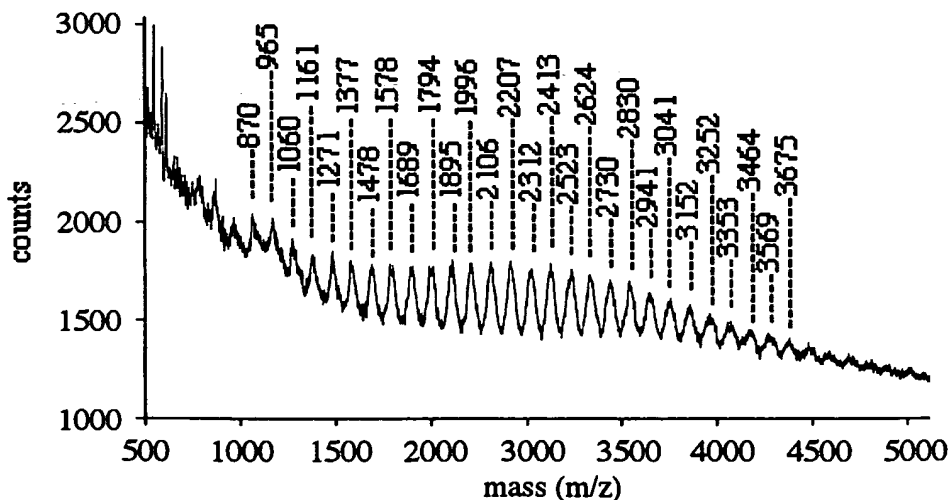
isobutyronitrile radical might be scavenged by **DPDTe** effectively to exclude the undesirable recombination and disproportionation reaction.

From the  $^1\text{H-NMR}$  spectrum of low molecular weight polystyrene ( $M_n=3\ 000$ ,  $M_w/M_n=1.17$  by GPC) obtained under  $[\text{DPDTe}]/[\text{AIBN}]=2$  (Figure 2), the molecular weight of the polymer was calculated to be 3 050 based on the integral intensities of methyl proton (in AIBN fragment) and methine proton (in the main chain), which was in good agreement with  $M_n$  by GPC indicating that the polymerization was entirely initiated by AIBN and the fatal chain termination or transfer reaction did not occur.



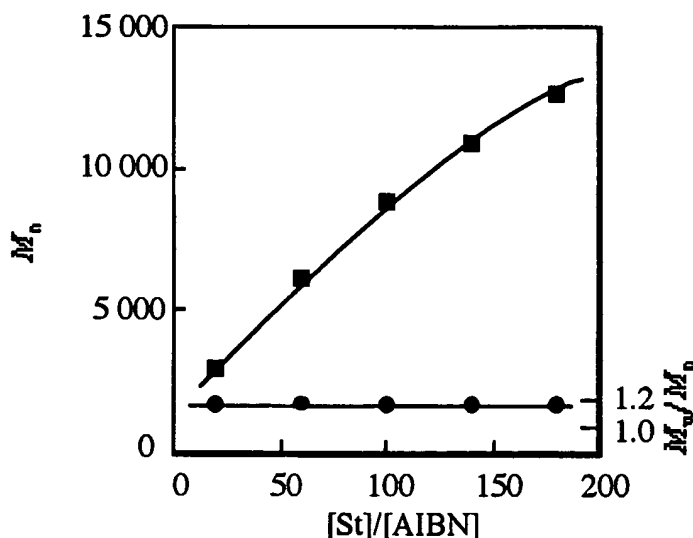
**Figure 2.**  $^1\text{H-NMR}$  spectrum of polystyrene ( $M_n=3\ 000$ ,  $M_w/M_n=1.17$ ) obtained at  $90^\circ\text{C}$  with AIBN/DPDTe initiating system

The low molecular weight polystyrene sample was further subjected to MALDI-TOF-Mass measurement, where all peaks were well separated by approximately  $104\text{m/z}$  in accord with the mass of repeating styrene unit (Figure 3). This result also strongly denies any side reaction throughout the polymerization.



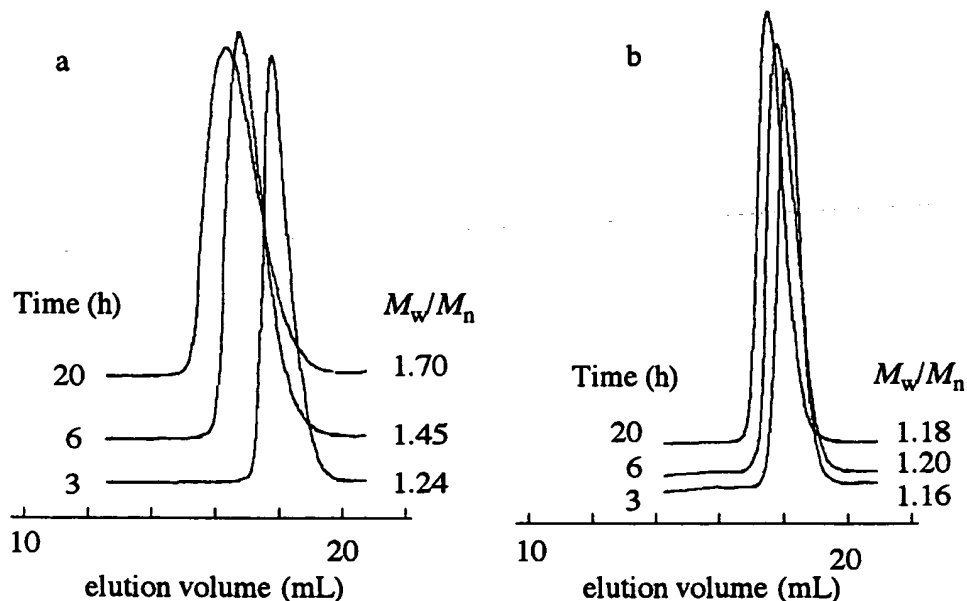
**Figure 3.** MALDI-TOF-Mass spectrum of polystyrene obtained by AIBN/DPDTe initiating system ( $M_n=3\ 000$ ,  $M_w/M_n=1.17$  by GPC)

The polymerization of styrene was likewise carried out with AIBN/DPDTe ([DPDTe]/[AIBN]=2) at 90°C for 36h under various [St]/[AIBN] ratio. Figure 4 shows the relationship between the monomer feed ratio and the polymer  $M_n$ , which is indicative of the well-controlled polymerization nature of the present system, that is,  $M_n$  can be predetermined by the monomer feed ratio and  $M_w/M_n$  are constantly narrow (below 1.18).



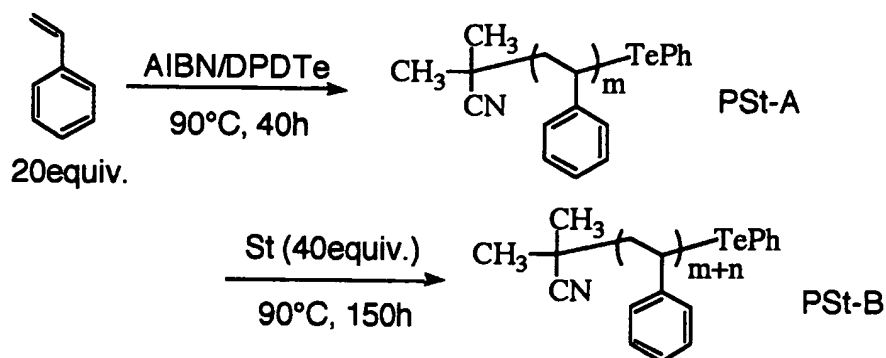
**Figure 4.** Relationship between [St]/[AIBN] and  $M_n$  ( $M_w/M_n$ )

The progress of the polymerization was subsequently monitored by GPC in systems without any initiator or with AIBN. Without initiator,  $M_w/M_n$  became broader at higher  $M_n$  region (Figure 5a). In sharp contrast,  $M_n$  increased keeping narrow  $M_w/M_n$  as the polymerization time went by when AIBN/DPDTe initiator was used, which also suggests the controlled character of the polymerization (Figure 5b).



**Figure 5.** GPC profiles in two polymerization systems  
a: [St]/[DPDTe]=100 at 125°C    b: [St]/[AIBN]/[DPDTe]=100/1/2 at 90°C

## Scheme 2.



Although the polymerization was found to be initiated only by AIBN to obtain polymers with the predictable  $M_n$ , the propagating end structure of the polystyrene is still obscure. The propagating end is expected to have benzyl telluride structure (See scheme in Figure 2), however, benzyl-tellurium bond are known to be unstable to decompose into  $\text{PhCHO}$ ,  $\text{PhCH}_2\text{OH}$ ,  $\text{PhCH}_3$ , and  $\text{PhCH}_2\text{CH}_2\text{Ph}$  with  $\text{O}_2$  and light [18]. In practice, peaks assignable to benzene ring adjacent to tellurium (ca. 7.8ppm) could not be clearly detected in  $^1\text{H}$ -NMR spectrum of polymers. Accordingly, the post-polymerization experiment was performed under nitrogen atmosphere in darkness to confirm the stability of the propagating end. Namely, the first polymerization of styrene (20equiv.) at 90°C for 40h was followed by the additional charge of styrene (40equiv.) in the second polymerization stage (Scheme 2). After the polymerization for 150h, a polymer (PSt-B) was obtained in 86% yield. From GPC analyses,  $M_n$  increased to higher mass region without any expansion of  $M_w/M_n$  compared to that of PSt-A, supporting the stability of the propagating end under these conditions (Figure 6).

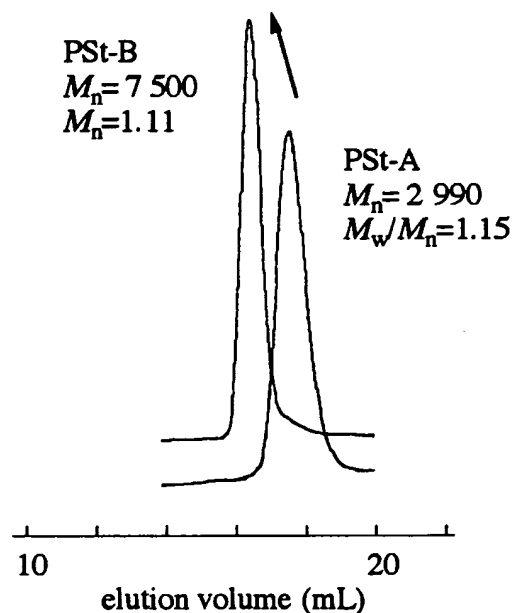


Figure 6. GPC profiles in postpolymerization experiment

Mechanistic discussion is still difficult from these data, however, it should be emphasized that the excellent radical capturing ability of DPDTe plays an important role in this polymerization system.

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